



A Theoretical Perspective on Strategies for Modeling High Performance Nonlinear Optical Materials

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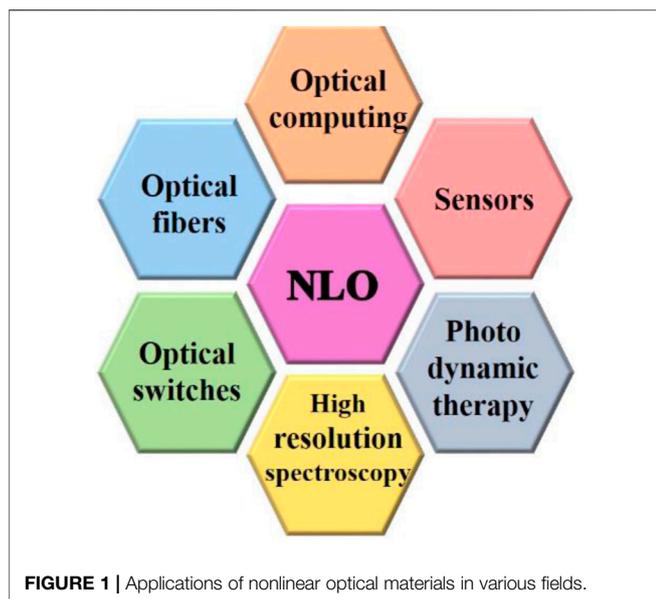
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Nonlinear optical (NLO) materials have spanned a large area of science and technology owing to their potential applications in optoelectronics. The invention of the first Ruby laser has sparked a fresh interest in the area of nonlinear optics. The computational designing and experimental synthesis of organic and inorganic NLO materials with higher order nonlinearities come into vogue in the field of materials science. To date, several strategies including metal ligand framework, push pull mechanism, diradical character, and so on have been devised to enhance the NLO response of materials. In addition, introduction of diffuse excess electrons is an efficient approach to design noncentrosymmetric materials for nonlinear optics. The current review highlights a systematic array of different computational studies (covering the last decade of intensive research work) for the theoretical designing of NLO materials. In the present review, theoretical designing from the simplest NLO material to the complex alkali, alkaline earth, transition, and superalkali doped nanomaterials is summarized. The emergence of excess electrons strategy has played a pivotal role in enhancing the NLO properties especially hyperpolarizabilities. We expect that this review will provide a better understanding of the NLO responses of nanoclusters, paving the way for the advancement of hi-tech NLO materials to meet the real challenges in optoelectronics.

Keywords: nonlinear optical materials (NLO), fullerenes, hyperpolarizability, electrides, alkalides

INTRODUCTION

Nonlinear optics is a new and versatile branch of science that describes the light-matter interaction when induced polarization nonlinearly depends on external electric and magnetic fields (Boyd, 2020; Shen, 1984). Nonlinear optical (NLO) phenomenon arises when a material generates electromagnetic radiations of varying phase, amplitude, and frequency during its propagation on interaction with electromagnetic fields (Tessore et al., 2018). The NLO effect is produced when strong electrical fields under high intensity laser beams interact with matter. In 1960, the invention of the first Ruby laser by Maiman sparked fresh interest in the field of nonlinear optics (Maiman, 1960).



Franken et al. also complemented this phenomenon by observing the second harmonic generation (SHG) effect in quartz crystals (Franken et al., 1961). The simple manifestations of nonlinear optics include intensity-dependent light refraction and absorption (Majumdar et al., 2020; Wang et al., 2018). The formation of solitons (Z. Luo et al., 2015), power restriction of light transmission (Lettow and Martin, 2010), and multiphoton fluorescence (Wostyn et al., 2001) are all possible outcomes of this phenomenon. The field of nonlinear optics has become a Frontier area in the fields of ultrafast pulse measurement (X. Liu et al., 2017), light generation and modulation (J. Chen et al., 2018), optical parametric amplification (Kumbhakar and Kobayashi, 2007; Popov and Shalaev, 2006), laser frequency conversion (D. Hou et al., 2018a), modulators (Grote et al., 2002), and optical switches (Biswal et al., 2019; W. Li et al., 2014). In addition, nonlinear optics have remarkable applications in dynamic image processing (Van Steenwinckel et al., 2001), sensing (Ray, 2010), high resolution imaging (Miller et al., 2002), optical computing (Hutchinson and Milburn, 2004), optical fiber communication (Arivuoli, 2001), optical data storage (Iliopoulos et al., 2010), and materials analysis (Y. R. Shen, 1989). The biological applications in the field of NLO microscopic imaging (Huff et al., 2008; Wang et al., 2009) or photodynamic therapy (Kachynski et al., 2014) are also of great interest. Some major applications of nonlinear optical materials are represented in **Figure 1**.

Bulk crystals such as potassium titanyl phosphate (KTP) (Stucky et al., 1989), beta-barium borate (β -BaB₂O₄) (Girisun et al., 2017), and lithium iodate (LiIO₃) (Kumar et al., 2010a; Kumar et al., 2010b) are currently used as commercial nonlinear media. NLO materials have covered a vast area of science and technology and many scientists are working on their exploration in various fields of optoelectronics. The increase in the number of publications year after year, approaching almost 570 papers in 2021, is evidence of the considerable efforts in the field of

nonlinear optics. A bar graph showing the number of publications for the last 5 years is shown in **Figure 2**. The current state of technology necessitates a strong demand for on-chip integration of photonic and optoelectronic devices.

Background of Nonlinear Optics

The history of nonlinear optics can be traced by the work of John Kerr on carbon disulfide (CS₂) crystals. He observed the alteration in the refractive index by induced quadratic electric field (E) and this phenomenon is known as the electro-optic Kerr effect (Kerr, 1879). In 1883, a similar but linear electric field effect was also observed in quartz and is now known as Pockel's effect (Burland, 1994). These nonlinear phenomena were only used in a limited way until the laser was invented in 1960, followed by the discovery of the second harmonic generation in quartz (Maiman, 1960; Franken et al., 1961). Based on these developments, the area of nonlinear optics exploded in the 1960s, with Bloembergen's pioneering research into the complete range of NLO responses of different materials (Armstrong et al., 1962; Ducuing and Bloembergen, 1964). A. D. Buckingham and co-workers have added a key contribution in developing understanding of NLO processes at the atomic and molecular levels (Buckingham and Orr, 1967).

The basic sources of microscopic hyperpolarizabilities were studied in depth during the 1970s. In 1973, the transmission of stationary NLO pulses in dispersive dielectric fibers was observed by Hasegawa et al. (Buckingham and Orr, 1967). The experimental methodologies for measuring these molecular nonlinearities, and fabricating novel crystals that could be useful in second-harmonic production and optoelectronic modulation have been devised (Gibbs et al., 1976; Mollenauer et al., 1980; Cirilo et al., 2010). In the early 1990s, second and third order NLO responses in atoms and small molecules were calculated and measured in the gas phase by David Shelton and Julia Rice (Shelton and Rice, 1994). David et al. worked on identification of chromophores with higher order optical nonlinearities using a range of electronic structural models and computational approaches (Kanis et al., 1992, 1994). This literature demonstrates that advanced computational methodologies on isolated atoms and molecules might help us to understand the origin of nonlinear processes and to contribute toward the designing tools for forecasting their features. Currently, a majority of the NLO work is focused on the causes, processes, and applications of NLO materials.

Basic Principle of Nonlinear Optics

Nonlinear optics illustrate the light-matter nonlinear relationship in a medium under the intense light beam (laser) and electromagnetic fields (Becker, 1998). On propagation of light through a medium, the valence electrons produce a charge transfer relative to the atoms in the medium under the action of induced electric field and results in medium polarization (P). The relationship between polarization intensity of medium and electric field strength of the incident light can be expressed as in **Equation 1**.

$$P = \epsilon_0 \chi^{(1)} E + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots \quad (1)$$

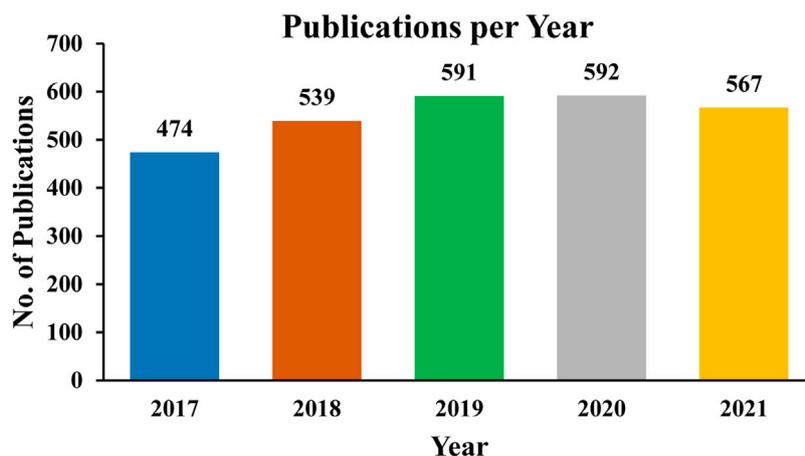


FIGURE 2 | Number of publications per year related to the theoretical studies on nonlinear optical materials: Data obtained by using keywords “Nonlinear optical, Theoretical” from Scopus as of November 2021.

Here, P is the macroscopic polarization strength, E is applied electric field strength, ϵ_0 is vacuum dielectric constant, $\chi^{(1)}$ is the first order linear susceptibility, $\chi^{(2)}$ is the second order nonlinear susceptibility, and so on. At the microscopic level, **Equation 1** can be written as

$$p = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (2)$$

Here, p is the microscopic polarization intensity of a molecule under electric field, α is the polarizability, β is first hyperpolarizability, γ is the second hyperpolarizability, and so on. In the presence of a weak electric field, higher order susceptibilities (from the second term and so on) can be neglected. As a result, polarization and electric field strength ($P = \epsilon_0 \chi E$) have a linear response making linear optics possible. Under the action of intense laser light, higher order susceptibilities from second to onward cannot be neglected. Therefore, NLO phenomenon occurs when the medium microscopic polarization p and macroscopic polarization P are nonlinearly proportional to the E (strength of the applied electric field). As a result, higher order NLO effect (second order NLO, third order NLO effect, and so on) have been observed in materials.

NLO response is not the property of all systems. In centrosymmetric systems, the induced polarization is the same in all directions and has no NLO response. Therefore, hyperpolarizability is zero in all directions in such systems. While in the case of non-centrosymmetric systems, the restoring force is determined by the charges of displaced electrons. The direction and amount of the applied electromagnetic field will also influence the induced polarization. As a result, materials that can generate an asymmetric wave can also produce an NLO response. Non-centrosymmetry is a basic requirement for a system to show an NLO response (Fan et al., 2010; Luo et al., 2018). All kinds of non-centrosymmetric systems exhibit NLO effects, but in order to obtain their potential applications, they must have a maximum

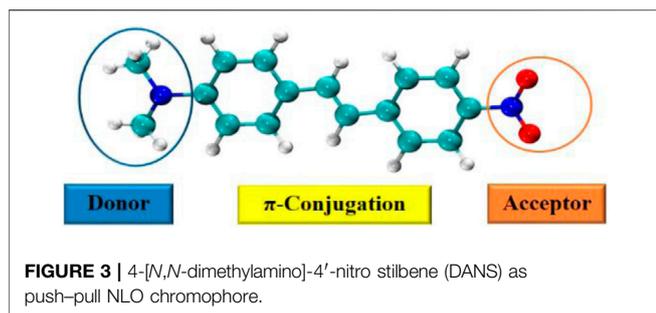
nonlinearity at low power. Therefore, the researchers have focused on designing novel materials with a higher order NLO response.

STRATEGIES FOR ENHANCEMENT OF NLO RESPONSE

A revolution in electronics is on the horizon with the uprising of two unique domains including spintronics and molecular electronics. Single-molecule magnets in spintronics can be used to establish a basic link between these two domains (Bogani and Wernsdorfer, 2010). Molecular optics may result by intriguing development in optics since the implementation and development of NLO materials at the molecular level. The NLO molecules can be used to make macroscopic NLO materials (Cheng et al., 1991; Delaire and Nakatani, 2000). Due to the discovery and diverse applications of nonlinear optics, the researchers are focused on improving the NLO response of various inorganic and organic materials by using a variety of strategies. To date, several approaches for tuning the NLO response of materials have been established. These include electron donor to acceptor push-pull mechanisms, designing octupolar molecules, introducing diffuse excess electrons, using multi-decker sandwich clusters, applying bond length alteration theory, designing metal organic frameworks (MOFs), and so forth. Some of these are listed here.

Electron Push-Pull Mechanism

The electron push-pull strategy was first introduced by Zyss and his co-workers (Zyss and Ledoux, 1994). This approach is primarily employed for organic chromophores especially stilbenes, porphyrins, paracyclophanes (Vijayakumar et al., 2008; Orbelli Biroli et al., 2011), and so on. The structure of such organic compounds is a major contributor toward the development of NLO response. When the donor-acceptor



groups are connected via π -bonding, a conjugated (D- π -A) system is formed. This system is referred to as a push-pull mechanism based system because of the intermolecular charge transfer (ICT) from donor to acceptor (linked through π -bonding), which leads to induction of polarization under the presence of light and electric field. The best example of such NLO chromophores is DANS (4-[N,N-dimethylamino]-4'-nitro stilbene) which shows an intramolecular charge transfer (ICT) (Vijayakumar et al., 2008). It has an electron donor dimethylamino group (-N(CH₃)₂) and nitro group (-NO₂) as electron acceptor with *trans*-stilbene as π -conjugated bridge as shown in **Figure 3**. Vijayakumar et al. observed that planar conformations would result in increased NLO activity (435.41×10^{-31} esu), but a departure from planarity results in decreased NLO activity (285.16×10^{-31} esu).

Paracyclophane (pCP) is an important building block for complexes in which D-A substituents interact via a sterically restricted (π - π) stack. In 2000, Zyss et al. observed the experimental and theoretical quadratic hyperpolarizability tensor (60×10^{-30} esu) of dipolar 4-(4-dihexylaminostyryl)-16-(4-nitrostyryl)[2.2]paracyclophane for the first time. The collective electron oscillator (CEO) approach was used to confirm collective nonlinear polarization involving the entire end-to-end molecular structure (Zyss et al., 2000). Since then, paracyclophanes are serving as novel NLO candidates in various fields. Recently, the NLO response of [2.2]paracyclophane based polymers has been investigated theoretically (Ivonina et al., 2020). The NLO properties of a series of diacetylene-functionalized organic molecules (DFOM) with D- π -A stacking have been computed. These complexes were designed by structural tailoring of newly synthesized BDDA (4,4'-(buta-1,3-diyne-1,4-diyl) dianiline) chromophores. The involvement of extended conjugation and charge transfer character have been explored via different DFT methods. The enhanced NLO response ($\beta = 2.5 \times 10^4$ au) of the designed diacetylene-functionalized organic complexes reflected that these complexes could serve as better NLO candidates (Khalid et al., 2019). The development of novel synthetic and theoretical techniques leads to more diverse substitution patterns of porphyrin rings because it widens the potential applicability in nonlinear optics. In this regard, NLO response of a series of substituted zinc(II) porphyrinates with -N(CH₃)₂ as donors and -NO₂ as electron acceptors has been investigated. The experimental and theoretical investigation of a series of 5,15 push-pull meso-diarylzinc(II) porphyrinates with -OCH₃ or -N(CH₃)₂ as donors and -COOH or -COOCH₃ as

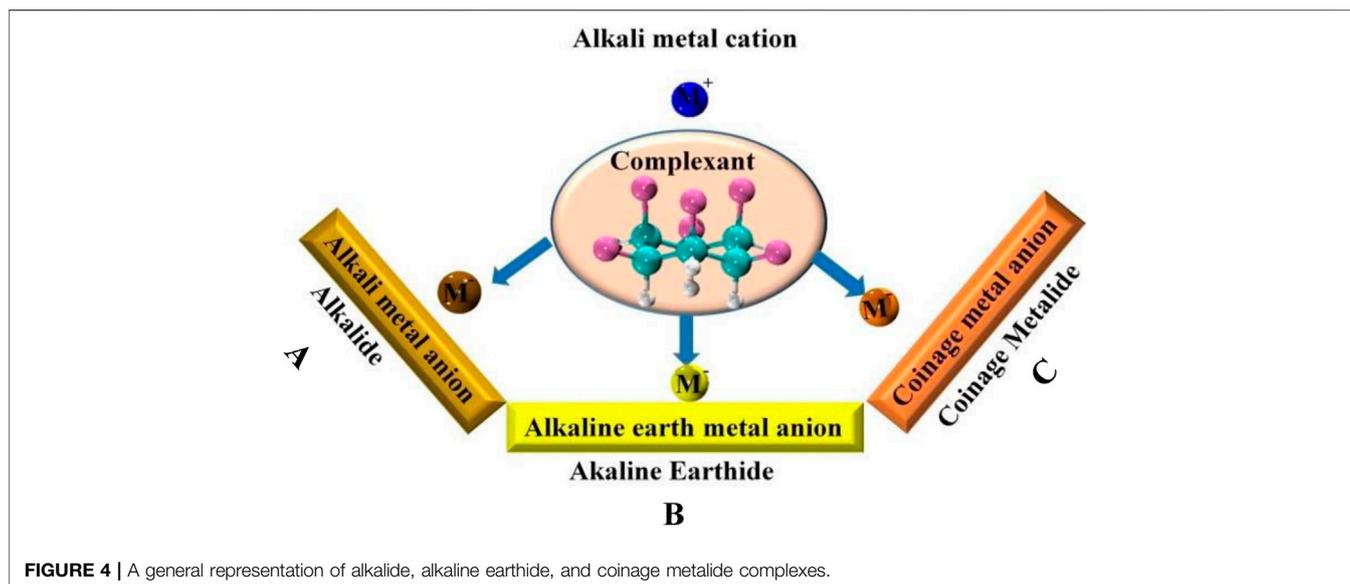
electron acceptors in DMF and chloroform have been explored (Orbelli Biroli et al., 2017). Their NLO response was determined using the electric-field-induced second-harmonic generation technique.

Metal Ligand Framework

Metal organic frameworks, a fascinating class of hybrid NLO materials, have resulted by altering the central metal atom or adjusting the organic linkers (with different functional groups) as compared to traditional organic and inorganic NLO crystals. According to a recent research on ZIF-8 (zeolitic imidazolate) framework (Van Cleuvenbergen et al., 2016), it is observed that ZIF-8 has a strong SHG signal that is similar to the inorganic crystals of KH₂PO₄. A theoretical investigation on the structures and exploration of NLO response of experimentally synthesized Zr-based UiO-66 MOFs with BDC (1,4-benzene-dicarboxylate) linkers and its substituents (-NH₂, -OH, -SH, and halogen atoms) has been carried out to reveal the effect of ligand functionalization on NLO properties (Ni et al., 2020). Recently, the NLO response of titanium-based MIL-125 MOFs (crystals) has been investigated using DFT calculations. In this MOFs, the BDC linkers have been altered either by extending the BDC ligands or by substituting various functional groups as in MIL-126 and MIL-127. It was observed that the NLO response especially SHG intensity has been improved on introducing substituent groups into the BDC linker (Ni et al., 2019). These findings are helpful for developing novel NLO materials with hi-tech performance.

Diradical Character

Diradical character is an efficient approach for the enhancement of NLO response of open-shell singlet systems (Nakano et al., 2004, 2007; Nakano et al., 2006b). The chemical systems with intermediate diradical character exhibit greater NLO response (hyperpolarizabilities) than pure or closed shell diradical systems. The cause of this reliance has been speculated by using the VCI (valence configuration interaction) approach for H₂ model (a two-site diradical system) (Nakano et al., 2006b) and a linear H₄ model for tetradiradical systems (Nakano et al., 2012). Several DFT calculations have been performed to investigate the relationship between hyperpolarizabilities and diradical character (γ) of singlet diradical systems such as *p*-quinodimethane (PQM) molecule (Nakano et al., 2005), polycyclic diphenalenyl radicals (Ohta et al., 2007), graphene nanoflakes (Nakano et al., 2008), and imidazole ring based diradical systems (Nakano et al., 2006a; Qiu et al., 2008). Apart from these studies, a comparison of NLO response of cyclic/linear acenes vs. phenylenes has reflected a distinct enhancement in the tetradiradical nature of cyclacenes as well as their second hyperpolarizabilities ($\gamma_{zzzz} \approx 10^4$ au) (Muhammad et al., 2013). These theoretical predictions have been observed in the TPA (two-photon absorption) analysis of experimentally synthesized diphenalenyl diradical compounds (Kamada et al., 2007), hepta/octazethrenes (Li et al., 2012), and benzannulated Chichibabin's hydrocarbons (Zeng et al., 2012), as well as in the THG (third harmonic generation) effect of BDPI-2Y (1,4-bis-(4,5-diphenylimidazole-2-ylidene)cyclohexa-2,5-diene) (Kishida



et al., 2010). Muhammad et al. theoretically observed the dependence of NLO response on the diradical character of various fullerenes (C_{20} , C_{26} , C_{30} , C_{36} , C_{40} , C_{42} , C_{48} , C_{60} , and C_{70}). It was observed that C_{20} , C_{60} , and C_{70} were closed-shell systems while others were intermediate and open-shell systems. The larger second order hyperpolarizabilities were observed for fullerenes with intermediate diradical character such as C_{40} have shown γ_{zzzz} up to 43.44×10^3 au. Similarly, the NLO responses of diradical character based various buckyferrocenes have been explored at the molecular level. The closed-shell buckyferrocenes were $(CpFe)_{2/5}C_{60}Me_{10}$ and $(CpFe)_2\eta^5C_{70}Me_{10}$, intermediate open-shell singlets were $(CpFe)_2\eta^5C_{70}Me_8$ ($CpFe)_2\eta^5C_{30}$, and $(CpFe)_2\eta^5C_{70}Me_4$ while others were purely open shell based complexes. The largest third order NLO response ($\gamma_{zzzz} = 130.71 \times 10^4$ au) was observed for $(CpFe)_2\eta^5C_{70}$ buckyferrocenes with intermediate diradical character (Muhammad et al., 2015). These findings show that diradical character has enhanced the NLO response of complexes and served as a suitable approach for obtaining high performance NLO materials.

EXCESS ELECTRONS STRATEGY

Introduction of excess electrons into various systems is a novel approach that remarkably enhances their NLO properties. The NLO response of organic and inorganic systems can be boosted by excess electrons. In 2004, Li et al. introduced a new potential class of NLO materials with diffuse excess electrons for the first time (Li et al., 2004). They investigated theoretically the nonlinear optical response of $(FH)_2\{e\}(HF)$ clusters with the highest hyperpolarizability of 8.1×10^6 au. Similarly, first hyperpolarizability ($\beta \approx 10^7$ au) of excess electron bound water trimer anion $(H_2O)_3^-$ was extremely larger than molecular cluster of water trimer $(H_2O)_3$ itself (W. Chen

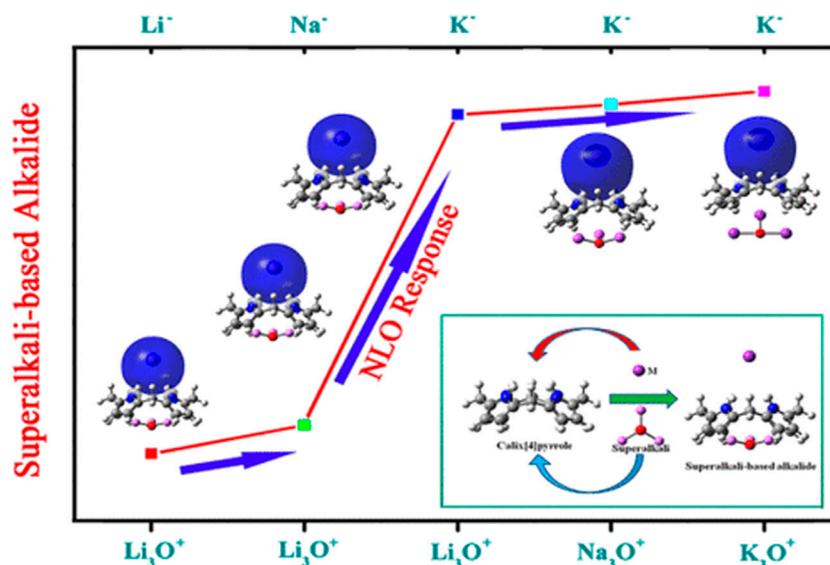
et al., 2004). These results indicate that the excess electrons have a potent role in improving the nonlinear optical features. A dispersive orbital is occupied by the diffuse excess electrons, which is in a Rydberg-like state. The nonlinear optical susceptibilities of a Rydberg atom or molecule are extremely high in the gas phase, as evidenced by available experimental data and theoretical studies (Manykin, 2002). The significant impact of excess electrons on clusters' hyperpolarizability opened new possibilities for the design and preparation of innovative NLO molecular materials. Doping of metal atoms (alkali, alkaline, transition) on complexants is an efficient approach to obtain excess electrons compounds (Ahsan and Ayub, 2020b; Munsif et al., 2018; Rad and Ayub, 2018c; Sun et al., 2017a). Electrides, alkalis, alkaline earthides, coinage metalides, and superalkalides are the various classes of excess electron compounds that show remarkable NLO response. A general representation for alkali, alkaline earthide, and coinage metalide complexes is shown in **Figure 4**.

Electrides

Electrides are a representative type of diffuse excess electron compounds that have a great possibility to serve as NLO materials. They are formed when valence electrons of metal atom are pushed by complexants and become excess electrons in the system. Dye et al. synthesized the first electride $Cs^+(18\text{-crown-6})_2e^-$ as an excess electron system in 1983 (Ellaboudy et al., 1983; Dawes et al., 1986). In 2005, Chen et al. theoretically investigated the NLO response of $(HCN)_n\text{-Li}$ and $\text{Li}-(HCN)_n$ ($n = 1, 2, 3$) electrides for the first time (W. Chen et al., 2005b). The 2s valence electrons of Li have become excess electrons by the interaction of a Li atom and $(HCN)_n$. Since then, many alkali metal based electride complexes with larger NLO response have been investigated. Electrides include cup-like $\text{Li@calix}[4]\text{pyrrole}$ (W. Chen et al., 2005b), M@pyrrole ($M = \text{Li, Na, and K}$) (Yu et al.,

TABLE 1 | Some excess electron based electrider complexes with enhanced NLO response.

Complex	Hyperpolarizability (au)	Software	Level of theory	References
Li@calix [4]pyrrole	7.3×10^3	Gaussian	B3LYP/6-311++G for (C,H,N) 6-311++G (3df, 3pd) for Li	W. Chen et al. (2005b)
$M_3O^+(e@C_{20}F_{20})^-$	1.3×10^4	Gaussian	CAM-B3LYP/6-311+G(d)	J.-J. Wang et al. (2012)
$K@r_6-Zn_{12}O_{12}$	1.0×10^5	Gaussian	LC-BLYP/6-311+G(d)	S. Khan et al. (2021b)
$Li_4N@Al_{12}P_{12}$	6.3×10^4	Gaussian	CAM-B3LYP/6-311++G (2days,2p)	Ullah et al. (2019b)
$Li_2F@B_{12}P_{12}$	3.4×10^5	Gaussian	LC-BLYP/6-31+G(d)	Ullah et al. (2019a)
$Li_n-H-(CF_2-CH_2)_3-H$	7.7×10^4	Gaussian	MP2/6-31+G(d) for (C,H,F) 6-311+G (3df) for Li	H. L. Xu et al. (2007)
K-TIMA	1.1×10^7	Gaussian	MP2/6-31+G(d) for (C,H,N) 6-311+G (3df) for (Li, Na and K)	H.-L. Xu et al. (2011)
$Li@B_{10}H_{14}$	2.3×10^4	Gaussian	MP2/6-31+G(d)	Muhammad et al. (2009)
$Li-H_3C_4N_2 \cdots Ca$	2.7×10^5	Gaussian	MP2/6-311++G (3df, 2pd)	Y.-F. Wang et al. (2014)
$Li@F_6C_6H_6$	7.1×10^5	Gaussian	MP2/ 6-31+G(d)	N. Hou et al. (2018c)
C_6Li_6-K	5.4×10^5	Gaussian	CAM-B3LYP/ 6-311+G(d)	Srivastava, (2020)
$C_6Li_6-Li_3O$	9.9×10^5	Gaussian	ω B97XD/ 6-311++G (2days,2p)	Ullah et al. (2020a)
$K_2^+TCNQ^-$	3.0×10^4	Gaussian	ROMP2/ 6-311++G for (C,H,O) 6-311++G (3df,3pd) for (Li, Na and K)	Li et al. (2009b)

**FIGURE 5** | Superalkali based alkalides of $Li_3O^+(\text{calix [4]pyrrole})M^-$ and $M_3O^+(\text{calix [4]pyrrole})K^-$ complexes. Reprinted from W. M. Sun et al., 2014 with permission from Copyright (2014) American Chemical Society.

2011), $M^+(e@C_{20}F_{20})^-$ (J.-J. Wang et al., 2012), and $(M_3O)^+(e@C_{20}F_{20})^-$ and chain-like $Li_n-H-(CF_2-CH_2)_3-H$ ($n = 1, 2$) (H.-L. Xu et al., 2007), and so on. Some of these electrideres are listed in **Table 1**.

Alkalides

Alkalides are novel excess electron compounds obtained when another metal atom is placed on the opposite side of electrideres. Complexants' excess electrons are wrapped around a second

metal atom to form a metal anion. Due to its low electron affinity, the excess electrons of anionic metal atoms are loosely bound with a dispersive nature. The first alkalide was successfully synthesized by Dye and co-workers in 1974 (Dye et al., 1974; Tehan et al., 1974). Later on, two stable alkalides $K^+(\text{Me}_6\text{Aza222})Na^-$ and $K^+(\text{Me}_6\text{Aza222})K^-$ were synthesized by the same group which opened up the possibility of alkalide applications (Kim et al., 1999). Theoretical studies of room temperature stable alkalides $Li^+(\text{calix [4] pyrrole})M^-$ with a greater NLO response

TABLE 2 | Nonlinear optical response (hyperpolarizability) of excess electron based alkalide complexes.

Complex	Hyperpolarizability (au)	Software	Level of theory	References
Li ⁺ (calix [4]pyrrole)K ⁻	2.4 × 10 ⁴	Gaussian	B3LYP/6-311++G for (C,H,N) 6-311++G (3df) for (Li, Na and K)	Chen et al. (2006)
(K+@2 ⁶ adz)K ⁻	3.2 × 10 ⁵	Gaussian	B3LYP/6-311++G for (C,H,N) 6-311++G (3df) for (Li, Na and K)	F.-F. Wang et al. (2008)
Li ⁺ (NH ₃) ₄ M ⁻	1.8 × 10 ⁵	Gaussian	MP2/6-311++G for (N,H) 6-311++G (3df) for (Li, Na and K)	Jing et al. (2006)
Ca(NH ₃) ₆ NaCl	1.2 × 10 ⁵	Gaussian	CAM-B3LYP/6-311++G (d,p)	W.-M. Sun et al. (2015)
K ₃ O ⁺ (calix [4]pyrrole)K ⁻	3.4 × 10 ⁴	Gaussian	CAM-B3LYP/ 6-311++G (d, p)	W. M. Sun et al. (2014)
OLi ₃ -K-OLi ₃	1.9 × 10 ⁴	Gaussian	MP2/6-311 + G(d)	Srivastava and Misra, (2017)

opened a fresh approach for developing innovative alkalides (W. Chen et al., 2005a). The alkalide complexes of Li⁺ (calix [4] pyrrole)K⁻ (W. Chen et al., 2006; Sun et al., 2013) and (M⁺@ n⁶adz)M⁻ (n = 2, 3, M, M' = Li, Na and K) (F.-F. Wang et al., 2008) with larger NLO response have been reported. Similarly, theoretical studies on smaller alkalides Li⁺(NH₃)₄M⁻ were explored (Jing et al., 2006). It was observed that the NLO response of smaller alkalides was four times larger than larger organic Li⁺(calix [4]pyrrole)M⁻ alkalides (Jing et al., 2006). A series of alkaline earth based alkalides M(NH₃)₆NaCl and M(NH₃)₆Na₂⁻ (M = Mg and Ca), with the highest hyperpolarizability up to 123,050 au have been explored theoretically (W.-M. Sun et al., 2015). Theoretical exploration of the NLO response of a new series of superalkali based alkalides Li₃⁺(calix [4]pyrrole)M⁻, Li₃O⁺(calix [4]pyrrole)M⁻, and M₃O⁺(calix [4]pyrrole)K⁻ (M = Li, Na, and K) has been carried out via DFT calculations with the highest first hyperpolarizability up to 34,718 au (W. M. Sun et al., 2014). The superalkali based alkalides are shown in **Figure 5**.

Similarly, superalkali (Li₂F, Li₃O, Li₄N, and Li₃) doped (aza222)K alkalides with enhanced NLO response have been investigated theoretically (W.-M. Sun et al., 2016b). Coinage metal (Cu, Ag, and Au) based alkalides of (M@3⁶adz)M⁻ have been investigated via DFT calculations and exhibit enhanced NLO responses (W. M. Sun et al., 2017a). A theoretical investigation of Li₂F superalkali based alkalides FLi₂-M-Li₂F (M = Li, Na, and K) has been carried out (Srivastava and Misra, 2015b). The negative charge on the sandwiched alkali metal atoms confirmed their alkalide nature. The mean polarizabilities of these stable superalkali based alkalides are up to 10³ au and hence may serve as better NLO candidates. The NLO response of Li₃O based alkalides OLi₃-M-OLi₃ (M = Li, Na, and K) have been observed theoretically for the first time (Srivastava and Misra, 2017). The sandwiched Li, Na, and K metal atoms bear a negative charge donated by excess electrons of superalkalis. The highest NLO response of 1.9 × 10⁴ au is observed for OLi₃-K-OLi₃ at C_{2v} symmetry.

Recently, a series of novel alkalides M⁺·I·M⁻ (M, M' = Li, Na, K) of a facially polar C₆H₆F₆ molecule (C₆H₆F₆ = **1**, all-cis-1,2,3,4,5,6-hexafluorocyclohexane) has been investigated theoretically (Sun et al., 2017b). These alkalides show remarkable NLO response with the highest hyperpolarizability of 1.45 × 10⁶ au. These findings were a tour de force of NLO

materials and paved the way to new possibilities for designing stable alkalides. The NLO response (hyperpolarizability) of some excess electron based alkalides are listed in **Table 2**.

Alkaline Earthides

Alkaline earthides are novel excess electron compounds in which electron acceptors are alkaline earth metals (alkaline earth anion) in place of alkali metals. They show very large NLO response and have partial p-electrons participation in excess electron formation, unlike alkalides in which partial s-electrons participate. Development of negative charge on alkaline earth metals in the presence of alkali metals is more difficult due to their ns² (closed shell) electronic configuration and their weak electron affinity. As a result, selecting the right complexant to stabilize the alkali metal cation and alkaline earth metal anion at the same time is critical. One such alkaline earthide organic system Li⁺·I·M (I = C₆H₆F₆ (all-cis-1,2,3,4,5,6-hexafluorocyclohexane) with Be, Mg, and Ca as an electron acceptor has been reported (Hou J. et al., 2018). Sajjad et al. carried out theoretical investigation of thermally stable alkaline earthides of M⁺·I·M' (I = C₆H₆F₆ (all-cis-1,2,3,4,5,6-hexafluorocyclohexane). These complexes have large NLO response with the highest hyperpolarizability up to 4.14 × 10⁹ au (Sajjad et al., 2020).

Ahsan et al. theoretically investigated the NLO response of two series of a novel organic M⁺(2⁶Adz)M⁻ (M⁻ = Be, Mg and Ca) alkaline earthides. These complexes show remarkable NLO response up to 1.0 × 10⁶ au (Ahsan and Ayub, 2020a). Zhu et al. reported alkaline-earthides of Li(NH₃)₄M (M = Be, Mg, Ca) based on a cage-like complexant. These complexes have an Li⁺ cation near the center of the complexant and the alkaline-earth anion is present outside. These alkaline earthides exhibit larger NLO response up to 8.01 × 10⁶ au and could be considered as novel NLO molecules (Zhu et al., 2019). Another example of alkaline earthide complexes based on hexaammine complexant M⁺(NH₃)₆M⁻ (M⁺ = Li, Na, K; M⁻ = Be, Mg, Ca) that show larger NLO have been investigated by Ahsan et al. (Ahsan and Ayub, 2020b). These complexes have remarkable NLO response up to 6.4 × 10⁵ au and were thermodynamically stable. Recently, the NLO response of superalkali containing alkaline earthides M₃O⁺·I·M⁻ (I = C₆H₆F₆; M⁻ = Be, Mg, Ca and M = Li, Na, and K) has been explored. The highest first hyperpolarizability is up to 5.2 × 10⁶ au and shows that designed complexes would have potential applications in optoelectronics (Bano et al., 2022).

Coinage Metalides

Coinage metalides are new representatives of excess electron compounds in which coinage metal atoms [copper (Cu), silver (Ag), and gold (Au)] serve as excess electron acceptors. The ns^1 valence-electron configurations and higher electron affinities (EA) were main features of coinage metal atoms than alkali metal atoms. Therefore, it is highly expected that the coinage metal atoms would be used to produce a new type of stable NLO material. In this regard, designing of a series of all-cis-1,2,3,4,5,6-hexafluorocyclohexane based $M^+-I-M'^-$ ($I = C_6H_6F_6$, $M' = Cu, Ag, \text{ and } Au$ and $M = Li, Na, \text{ and } K$) complexes have been investigated, theoretically. These complexes were thermodynamically stable due to stronger electrostatic interactions. All these coinage metalides possess remarkably enhanced NLO response up to 90,220 au (X.-H. Li et al., 2020a).

Superalkalides

The excess electron compounds in which a superalkali bears the anionic site are termed superalkalides. The larger volume of superalkalides than alkalides results in loosely binding of excess electrons to the superalkali core. It results in a more diffuse and readily polarized electron density distribution of complexes. Therefore, superalkalides might be responsible for the enhancement of NLO response. It is more difficult to locate an acceptable complexant to synthesize superalkalides due to the more loosely bounded nature of excess electron in superalkalis. The complexant in superalkalides must be highly resistive toward reduction. In 2015, the designing of the first superalkalides $M^+(en)_3M_3'O^-$ ($en = \text{ethylenediamine}$; $M, M' = Li, Na, \text{ and } K$) was carried out by the aid of *ab initio* calculations. These superalkalides were stabilized by the presence of hydrogen bonds and have remarkable NLO response (Mai et al., 2015). Similarly, designing superalkalides $L-M-L-M'_3O$ ($L, C_6H_6F_6$) has been investigated theoretically (B. Li et al., 2018). It was observed that designed superalkalides $L-M-L-M'_3O$ were thermodynamically more stable than their respective alkalides. Moreover, these superalkalides possess larger NLO response up to 1.31×10^6 au for $L-Li-L-Li_3O$ complex and would be useful candidates for high performance NLO materials.

Supersalts

Superalkalis in combination with superhalogens result in the formation of supersalts such as Li_3O , Cs_2NO_3 , and Cs_2Cl (superalkalis) in combination with BeF_4 , BeF_3 , and NO_3 (superhalogens) constitute supersalts (Giri et al., 2014). Wang et al. theoretically observed superhalides of $(Li_3)^+(SH)^-$ ($SH = LiF_2, BeF_3, \text{ and } BF_4$). These superalkali-superhalogen compounds have special characteristics of low vertical ionization energy, delocalized σ bonding orbital on the Li_3 ring and are electriles or alkalides in nature (F. Wang et al., 2006). The theoretically calculated bond energies of Li_6B-X ($X = F, LiF_2, BeF_3, BF_4$) supersalts are up to 220.6 kcal/mol with enhanced NLO response ranging from 5166.5 to 17,791 au (Li et al., 2008). Similarly, the supersalts of BF_4-M ($M = Li, FLi_2, OLi_3, NLi_4$) have been investigated theoretically (Yang et al., 2012). The NLO response and binding energies of these ionic compounds are also higher than pure superalkalis.

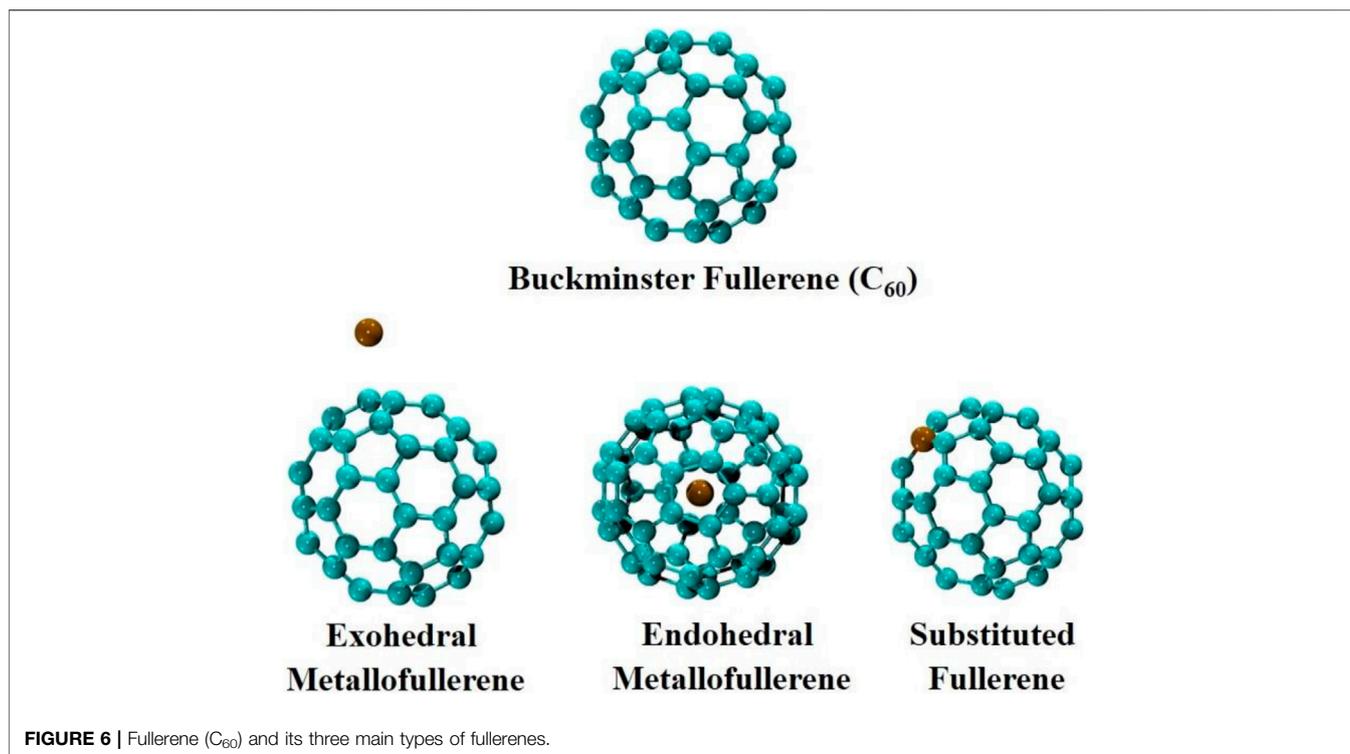
EXCESS ELECTRON BASED SYSTEMS IN NONLINEAR OPTICS

Many organic and inorganic excess electron based NLO materials have been designed theoretically. Doping is an efficient approach to enhance the NLO response of various systems including cyclacene (Xu et al., 2009), calix [4] pyrrole (W. Chen et al., 2006), organic and inorganic fullerenes (Ahsan et al., 2021; S.; Liu et al., 2019; Shakerzadeh et al., 2016a; Ullah et al., 2020b), phosphorenes, $B_{10}H_{14}$ baskets (Muhammad et al., 2009), cyclic polyamines (Li et al., 2009a), fluorocarbons (H. L. Xu et al., 2007), and so forth.

Fullerenes

Kroto et al. invented fullerene, a third allotropic form of carbon, in 1985 and were awarded the Nobel prize in 1996 for fullerene discovery (Kroto et al., 1985; Lopez et al., 2011). Fullerenes are sp^2 hybridized polyhedral carbon cages with resonating π electrons (Haymet, 1985; Haddon et al., 1986). Fullerenes exist in a variety of shapes, including hollow spheres, ellipsoids, and tubes depending on the amount of carbon atoms in them, for example, C_{20} , C_{60} , and C_{70} (Wakabayashi and Achiba, 1992; Ortíz-Saavedra et al., 1993; Friepertinger, 1996). Bucky balls, also known as spherical fullerene (C_{60}), is a stable carbon cluster with 20 hexagons and 12 pentagons that resemble a soccer ball (Hawkins et al., 1991). It has a hollow sphere like geometry with a diameter of 7 Å. It is stabilized by electron resonance and can tolerate extreme temperature and pressure conditions (Chuvilin et al., 2010). Fullerenes have attracted extensive attention in various fields including optoelectronics (Tutt and Kost, 1992), information technology (Senfleben et al., 2009), biomedical (Q. Liu et al., 2014; Markovic and Trajkovic, 2008; Stoilova et al., 2007), etc. In the area of nonlinear optics, various classes of fullerene family such as endohedral fullerenes, exohedral fullerenes, and substituted fullerenes have been explored as in Figure 6.

Exohedral fullerenes are the most versatile fullerenes. They are formed by the doping of atoms to the outside of the fullerene cage. In this regard, LaC_{60} has been synthesized and theoretically investigated (Rosen and Wästberg, 1989; Rosen and Waestberg, 1988). The exohedral nature of fullerenes was also observed in superconductive alkali fullerides general formula M_3C_{60} ($M = K, Rb, Cs$) (Erwin and Pickett, 1991; Pauling, 1991; Sparrn et al., 1991; Novikov et al., 1992). Endohedral metallofullerenes are formed by inside doping of metal atoms to a fullerene cage. Endohedral metallofullerenes were first predicted in 1985 by the encapsulation of the La^+ (lanthanum ion) in C_{60} (Heath et al., 1985). After the macroscopic manufacture of fullerenes in 1990, rapid research of its unique features became available (Krätschmer et al., 1990a; Krätschmer et al., 1990b). Polar endohedral metallofullerenes $Li@C_{60}$ have emerged as novel nanomaterials from its first synthesis reported in 1996 (Tellgmann et al., 1996). Later on, two of its salts $[Li^+@C_{60}]PF_6^-$ and $[Li^+@C_{60}]SbCl_6^-$ have been synthesized and were confirmed by crystallographic analysis (Okada et al., 2012). A theoretical investigation on $[Li@C_{60}]PF_6$ endofullerene complex has been carried out and its spectral properties match well with



the experimental data (Srivastava et al., 2016a). The endohedral metallofullerene complex of $Li@C_{60}-PF_6$ is resulted by the interaction of $Li@C_{60}$ with PF_6 superhalogen and shows a remarkable NLO response up to 1500 au. Similarly, NLO response of stable $Li@C_{60}-BX_4$ ($X = F, Cl, Br$) complexes have been explored theoretically (S.-J. Wang et al., 2013). Superalkali (Li_2F, Li_3O, Li_4N) entrapped C_{60} endofullerenes have been investigated theoretically and a comparison of their electronic properties with $Li@C_{60}$ has been carried out (Srivastava et al., 2016). These superalkali@ C_{60} endofullerenes are stabilized by charge transfer from superalkali toward C_{60} fullerenes and have large polarizabilities. Superalkali endofullerenes on interaction with superhalogens $SA@C_{60}-X$ ($SA = Li_2F, Li_3O, Li_4N, X = BF_4, BCl_4,$ and BBr_4) form stable endofullerene complexes (Srivastava et al., 2017). The nonlinear optical response has been computed for these complexes and the highest NLO response up to 3.2×10^4 au for $Li_2F@C_{60}-BBr_4$ has been computed. Fullerenes with encapsulated metal atoms have unique features that are not present in pristine fullerenes (A. A. Popov et al., 2013). Endohedral fullerene complexes have prospective applications in MRI contrast agents (Anilkumar et al., 2011; Zhang et al., 2007), radiotracers (Kobayashi et al., 1995), polymeric solar cells (PSCs) (Ross et al., 2009), lasers (Yakigaya et al., 2007), optoelectronics (B. Wu et al., 2015; Lee et al., 2002), and in quantum computers (Benjamin et al., 2006).

Substituted fullerenes, also known as hetero-fullerenes, have one or more carbon atom of fullerene replaced by heteroatoms. The first heterofullerene $C_{59}B$ was synthesized by Gou et al., in 1991 (Guo et al., 1991). Similarly, synthesis and electronic structure of five stable metallocarbohedrenes M_8C_{12} ($M = Ti,$

Zr, Hf, V) have been achieved by using anion photoelectron spectroscopy (S. Li et al., 1997). Since then, a variety of hybrid or non-carbon fullerene-like structures with varied numbers of substituted metal atoms ($Al_{12}N_{12}, B_{12}N_{12}, Al_{12}P_{12}, B_{12}P_{12}$ etc.) has also been reported (Akasaka et al., 1999; Billas et al., 2000; Liu et al., 2019; Paul et al., 2017) and is shown in **Figure 7**.

The replacement of $C=C$ double bonds with $X-Y$ hetero bonds is a viable technique for the development of stable heterofullerenes. The geometric, stability and electronic properties of C_{20} analogous-heterofullerenes $X_4Y_4C_{12}$ ($X = B, Al, Ga, Si$ and $Y = N, P, As, Ge$) have been investigated theoretically (Koochi et al., 2018). The homonuclear non-carbon nanocages may include gold (Gao et al., 2014; Zheng et al., 2018a) and boron nanocages (Z. Wang et al., 2020) while nitrides and phosphides of group III and carbides of group IV are included in heteronuclear non-carbon nanocages (Tahmasebi et al., 2016). The relative stabilities of different sized nanocages have been the subject of several theoretical investigations. Fowler et al. theoretically investigated that $B_{12}N_{12}$ is the most stable nanocage among $B_{12}N_{12}, B_{16}N_{16},$ and $B_{28}N_{28}$ nanoclusters (Seifert et al., 1997). The first synthesis of $B_{12}N_{12}$ nanocluster was carried out by Oku et al. and was detected by laser desorption time-of-flight mass spectrometry (Oku et al., 2004). Wu et al. explored a series of $(AlN)_n$ ($n = 2-41$) nanocages and concluded that $Al_{12}N_{12}$ inorganic fullerene is the most stable and served as a suitable NLO substrate (H.-S. Wu et al., 2003). Similarly, Beheshtian et al. explored the geometric and electronic properties of $Al_{12}N_{12}, B_{12}N_{12}, Al_{12}P_{12},$ and $B_{12}P_{12}$ fullerenes like structure via DFT simulations (Beheshtian et al., 2012). These nanostructures are

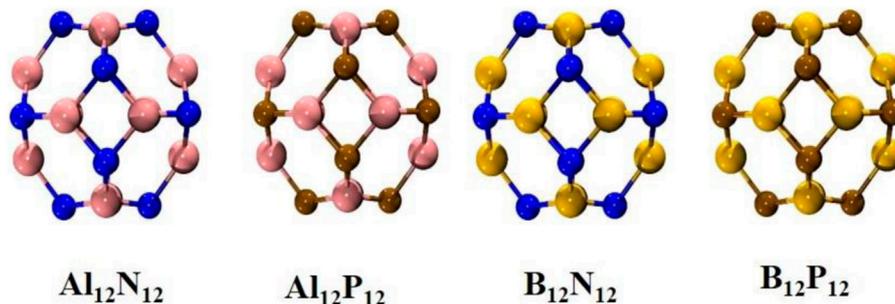


FIGURE 7 | Non-carbon fullerene like nanoclusters of $\text{Al}_{12}\text{N}_{12}$, $\text{Al}_{12}\text{P}_{12}$, $\text{B}_{12}\text{N}_{12}$, and $\text{B}_{12}\text{P}_{12}$.

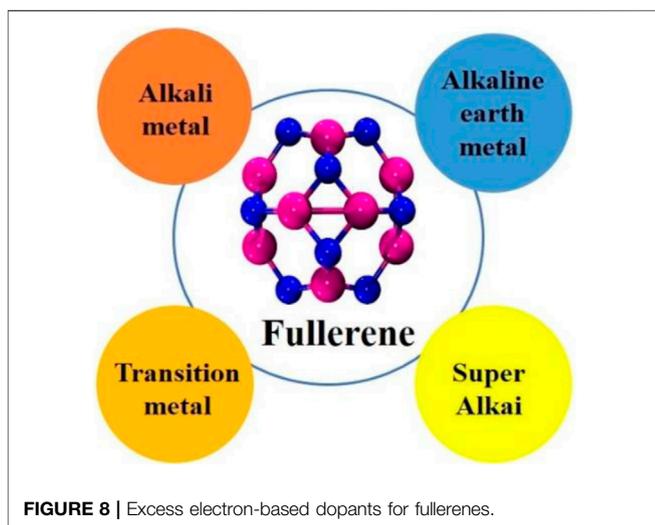


FIGURE 8 | Excess electron-based dopants for fullerenes.

semiconductor materials with a wide energy gap. Group III nitrides and phosphides with fullerene like properties come in a variety of sizes. The geometrical, electrical, and nonlinear optical properties of these fullerene-like structures were altered on heteroatom introduction. These nanocages can be doped by various electron-based systems as shown in **Figure 8**.

Alkali Metal Doped Nanocages

Introduction of diffuse excess electron is an efficient approach to improve the NLO response of various systems. Alkali metals can donate excess electrons easily due to low ionization potential (Redko et al., 2005). Fullerene like nanostructures of group II-VI and III-V ($\text{Al}_{12}\text{N}_{12}$, $\text{B}_{12}\text{N}_{12}$, $\text{Al}_{12}\text{P}_{12}$, $\text{B}_{12}\text{P}_{12}$, $\text{Be}_{12}\text{O}_{12}$, $\text{Mg}_{12}\text{O}_{12}$, $\text{Ca}_{12}\text{O}_{12}$, $\text{Si}_{12}\text{C}_{12}$, etc.) are important sources of nanoscale materials due to their potential applications as solar cells, optoelectronics quantum devices, hydrogen storage, photocatalysts, and in biomedicine (Rad and Ayub, 2018a; Zheng et al., 2018b; Ravaei et al., 2019; Zhou et al., 2019). The geometrical, electrical, and optical properties of these nanocages will be altered on the introduction of alkali metal. Niu et al. observed the alkali metal doping at various position of $M@x\text{-Al}_{12}\text{N}_{12}$ ($x = b_{66}$, b_{64} , and r_6). Diffuse excess electrons of alkali metals have lowered the energy gap that led to an

enhancement in NLO response of $\text{Al}_{12}\text{N}_{12}$. The highest β_2 of 8.89×10^5 au has been obtained for $\text{Li}@r_6\text{-Al}_{12}\text{N}_{12}$. It reflects that designed complexes will be applicable in hi-tech NLO materials and electronic nanodevices (Niu et al., 2014). Alkali metal doping at various position (b_{64} , and r_6) of $\text{Al}_{12}\text{N}_{12}$ nanocage is shown in **Figure 9**.

Alkali metal doping on $\text{Be}_{12}\text{O}_{12}$ and $\text{Mg}_{12}\text{O}_{12}$, the most viable clusters of group II-VI, has been reported. Their results show that alkali metal interaction with $\text{Be}_{12}\text{O}_{12}$ and $\text{Mg}_{12}\text{O}_{12}$ tuned up their structural and optoelectronic properties. A more pronounced NLO response was observed by exohedral doping and was larger than encapsulated ones for these metal oxide nanoclusters (Shakerzdeh et al., 2015). First synthesis of $\text{B}_{12}\text{N}_{12}$ nanocage and its detection by laser desorption mass spectrometry by Oku et al. opened new research perspectives in various fields (Oku et al., 2004). Theoretical investigation of alkali metals doped $\text{MB}_{12}\text{N}_{11}$ and $\text{MB}_{11}\text{N}_{12}$ has been carried out for their potential applications in nonlinear optics. The highest NLO response of 1.3×10^4 au for $\text{KB}_{12}\text{N}_{11}$ was obtained (Maria et al., 2016). In another work, structural stability, boundary crossing barriers, and NLO properties of alkali metals encapsulated $\text{X}_{12}\text{Y}_{12}$ nanocages ($X = \text{B}, \text{Al}$ and $Y = \text{N}, \text{P}$) have been studied. A correlation existed between the size of alkali metal with adsorption energies of complexes and diameter of nanocages with the distortion energies. It was concluded that the nonlinear optical properties of alkali metal encapsulated phosphide nanocages ($\text{B}_{12}\text{P}_{12}$) were two to three times larger than those of corresponding nitride nanocages. The highest NLO response was obtained for $\text{K}@ \text{B}_{12}\text{P}_{12}$ nanocage, i.e., 5.7×10^5 au due to its very low excitation energy (0.5 eV) (Ayub, 2016). In 2016, Hou et al. studied the structural and NLO response of alkali metal atoms doped $\text{B}_{12}\text{N}_{12}$ electrides via DFT simulations. It was observed that HOMO-LUMO energy gap of designed electrides was lowered by the introduction of excess electrons of alkali metals. The highest nonlinear optical response of 18,889 au was observed in $\text{B}_{12}\text{N}_{12}\text{-Na}$ isomer. The decrease in transition energy values in the range of 1.4–2.3 eV has caused the enhancement in NLO response (N. Hou et al., 2016).

Shakerzadeh and co-workers observed the electro-optical properties of Li complexation with $\text{B}_{12}\text{N}_{12}$ and $\text{B}_{16}\text{N}_{16}$ nanoclusters theoretically. It was concluded that Li complexation with boron nitride nanoclusters has significantly tuned up the nonlinear optical response with the reduction in

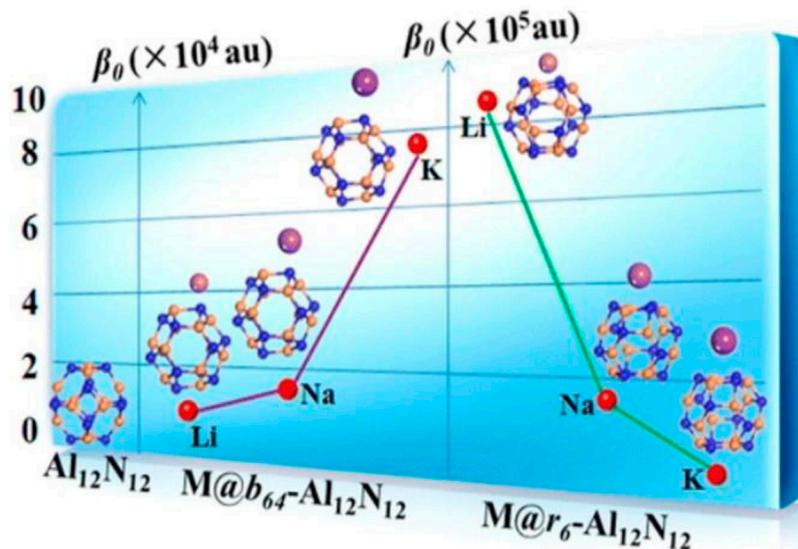


FIGURE 9 | Alkali metal doping at various positions of $M@x\text{-Al}_{12}\text{N}_{12}$ nanocage ($x = b_{64}$, and r_6). Reprinted with permission from Niu et al., 2014. Copyright (2014) American Chemical Society.

HOMO–LUMO energy gap. Large NLO response in the range of 2975–130,837 au reflected that the Li complexed boron nitride clusters could serve as innovative electro-optical materials (Shakerzadeh et al., 2016b). The same group observed the optoelectronic effect of alkali metals (Li, Na, and K) encapsulation on $\text{B}_{12}\text{N}_{12}$, $\text{Al}_{12}\text{N}_{12}$, $\text{Ga}_{12}\text{N}_{12}$, C_{24} , $\text{Si}_{12}\text{C}_{12}$, and $\text{Ge}_{12}\text{C}_{12}$ nanoclusters of group III nitrides and group IV carbides. Nitride nanoclusters show remarkable NLO response than that of corresponding carbides. Optoelectronic properties of $\text{B}_{12}\text{N}_{12}$ complexes especially hyperpolarizabilities were remarkably increased to 8505.49 au for $\text{Na}@_{\text{B}_{12}\text{N}_{12}}$ and 122,503.76 au for $\text{K}@_{\text{B}_{12}\text{N}_{12}}$ (Tahmasebi et al., 2016).

Alkali metal substituted $\text{MX}_{12}\text{P}_{11}$ and $\text{MX}_{11}\text{P}_{12}$ ($X = \text{B}, \text{Al}$) nanocages were also explored for geometric, electronic, and NLO properties investigation. Diffuse excess electrons of alkali metals ($M = \text{Li}, \text{Na}, \text{and K}$) have boosted up the NLO response of phosphide nanocages by the decrease in HOMO-LUMO energy gap (Maria et al., 2017). In the same year, Song et al. computed the optoelectronic properties of alkali metal doped $\text{C}_{24}\text{N}_{24}$ nanocage by using DFT calculations. Alkali metals were doped outside ($M = \text{Li}, \text{Na}, \text{and K}$) and inside ($M = \text{Na}$ and K) the nanocage at various doping positions. Alkali metal doping altered the electronic properties and orbital energy gap have lowered in both cases in contrast to pristine $\text{C}_{24}\text{N}_{24}$. The highest first hyperpolarizabilities obtained for $M_{\text{out}}@_{\text{C}_{24}\text{N}_{24}}$ and $M_{\text{int}}@_{\text{C}_{24}\text{N}_{24}}$ were 1242 au and 4772 au, respectively (Song et al., 2017). Stable $\text{Si}_{12}\text{C}_{12}$ nanocage has been observed theoretically and has many applications in optical communication, optical data storage, laser devices, and optical computing (Pochet et al., 2010; Javan, 2013; Duan and Burggraf, 2015). Theoretical investigation of alkali metals ($M = \text{Li}, \text{Na}, \text{and K}$) doping on $\text{Si}_{12}\text{C}_{12}$ nanocage was carried out. There was a remarkable enhancement in nonlinear optical response of $M@_{\text{Si}_{12}\text{C}_{12}}$

complexes as compared to pristine $\text{Si}_{12}\text{C}_{12}$ (Solimannejad et al., 2017).

Exploring novel NLO materials is an area of scientific investigation of our recent era. In this regard, $\text{Zn}_{12}\text{O}_{12}$ nanocage served as a stable motif with a potential for cluster materials (Reber et al., 2006). In a recent work, endohedral and exohedral doping of alkali metals on $\text{Zn}_{12}\text{O}_{12}$ clusters at all possible sites have been carried out. The DFT results manifest that most of $M@_{\text{Zn}_{12}\text{O}_{12}}$ complexes were electroneutral in nature and thermodynamically stable. Alkali metal doped $\text{Zn}_{12}\text{O}_{12}$ nanocages have prominent features of exothermic encapsulation superior to other inorganic nanocages with endothermic encapsulation. The energy gaps were significantly reduced with the enhancement in NLO response. The highest NLO response of 1.0×10^5 au was observed for $\text{K}@_{r_6}\text{-Zn}_{12}\text{O}_{12}$ complex. Third order NLO response was also computed for the designed $M@_{\text{Zn}_{12}\text{O}_{12}}$ electroneutral complexes (S. Khan et al., 2021b). Similarly, geometric, electronic, and NLO response of endohedral and exohedral alkali metal doped $\text{Ca}_{12}\text{O}_{12}$ electroneutral complexes have been studied. The excess electrons of alkali metals have caused reduction in energy gaps of these complexes. The highest NLO response of the order of 1.0×10^6 au was obtained for endohedral electroneutral complexes ($\text{endo-K}@_{\text{Ca}_{12}\text{O}_{12}}$) (Ahsan et al., 2021).

Recently, a DFT investigation of bi-alkali metals ($\text{Li}_2, \text{Na}_2, \text{K}_2$) doped $\text{B}_{12}\text{P}_{12}$ nanocages has proved to be an effective approach. These bi-alkali metals doped complexes were thermodynamically stable with enhanced NLO response of the order of 4.0×10^4 au. Non-covalent interactions and atoms in molecules analyses reflected their bonding phenomenon (Baloach et al., 2021). In other work, bi-alkali metal doped $\text{Al}_{12}\text{N}_{12}$ nanoclusters were explored with greater stability. A remarkable enhancement in the NLO response with the reduction in HOMO-LUMO energy gap was observed. The highest hyperpolarizability of 1.2×10^5 au

TABLE 3 | Alkali metal doped complexes with enhanced nonlinear optical responses.

Complex	Hyperpolarizability (au)	Software	Level of theory	References
Li@r ₆ -Al ₁₂ N ₁₂	8.8 × 10 ⁵	Gaussian	MP2/ 6-31+G(d)	Niu et al. (2014)
Li@Be ₁₂ O ₁₂	9.4 × 10 ³	Gaussian	CAM-B3LYP/ 6-311+G(d)	Shakerzdeh et al. (2015)
Li@Mg ₁₂ O ₁₂	2.7 × 10 ⁴	Gaussian	CAM-B3LYP/ 6-311+G(d)	Shakerzdeh et al. (2015)
K-B ₁₂ N ₁₁	1.3 × 10 ⁴	Gaussian	CAM-B3LYP/ 6-31+G(d)	Maria et al. (2016)
K@B ₁₂ P ₁₂	5.7 × 10 ⁵	Gaussian	CAMB3LYP/ 6-311+G(d)	Ayub, (2016)
Na@B ₁₂ N ₁₂	1.8 × 10 ⁴	Gaussian	MP2/ 6-31+G(d)	N. Hou et al. (2016)
Na@Si ₁₂ C ₁₂	5.7 × 10 ³	Gaussian	MP2/6-31+G(d)	Solimannejad et al. (2017)
K@Ca ₁₂ O ₁₂	1.0 × 10 ⁶	Gaussian	ωB97XD/ 6-31G (d,p)	Ahsan et al. (2021)

for K₂@N_{top}-Al₁₂N₁₂ reflected that these bi-alkali metal doped complexes proved as potential candidates in high-tech NLO materials (Sohail et al., 2021). The highest nonlinear optical response of some alkali metal doped nanocages is listed in **Table 3**.

Alkaline Earth Metal Doped Nanocages

Alkaline earth metals (Be, Mg, Ca, Sr, Ba, and Ra) are also a good source of excess electrons for complexes. In this regard, alkaline earth metal oxides especially BeO and MgO are wurtzite insulators, with very high thermal conductivity and melting points (Duman et al., 2009). Nonlinear optical response of alkaline earth metals doped Be₁₂O₁₂ and Mg₁₂O₁₂ nanocluster was studied. Excess electrons of alkaline earth metals have profoundly enhanced the NLO response of Be₁₂O₁₂ and Mg₁₂O₁₂ nanocages and their HOMO-LUMO gaps were lowered. The highest hyperpolarizability of the order of 4.72 × 10⁴ au was obtained for endo-Ca@Mg₁₂O₁₂. Hyperpolarizability trend was rationalized by two-level model calculations and β_{vec} was also computed (Kosar et al., 2020a). In another work, alkaline earth metals doping on (XY)₁₂ (X = Al, B, and Y = P) based phosphide nanoclusters of group III has been observed theoretically. Excess electrons of alkaline earth metals have lowered the HOMO-LUMO gaps of designed complexes and enhanced NLO response. The highest hyperpolarizability of the order of 7.8 × 10⁴ au was observed in this case (Ullah et al., 2020b). Similarly alkaline earth metals doping on Al₁₂N₁₂ nanocages was carried out by using DFT calculations. It was observed that designed complexes were thermodynamically stable, and their energy gaps (G_{H-L}) were significantly reduced. These designed complexes have the ability to serve as potential NLO candidates as they have large NLO response of 7769 au as compared to pristine Al₁₂N₁₂ (0 au) (Ullah et al., 2020c). Further exploration of NLO materials by single and multi-doping of odd number alkaline earth metals on C₂₀ fullerenes was carried out. The stable complex Ca₅@C₂₀ has the highest hyperpolarizability of 6.5 × 10⁷ au with the energy gap of 1.40 eV. These multi-alkaline earth metals doped complexes would be an ideal choice to obtain novel nanomaterials in optoelectronics (Tahir et al.,

2020). In other work, theoretical investigation of Be, Mg, and Ca (even number = 2, 4, 6) doped C₂₀ nanocluster have been carried out. The complexes were thermodynamically stable and the highest binding energy of -241.18 kcal mol⁻¹ was observed for Be₆@C₂₀. Their energy gap (G_{H-L}) was effectively reduced for all complexes with the lowest value of 0.82 eV for Ca₆@C₂₀ nanocluster. Their NLO response was also enhanced significantly but was lower than odd alkaline earth metal doped C₂₀ (Kosar et al., 2021b). Single and multi-alkaline earth metal atoms doping on C₂₄ fullerene have been carried out. The Be₄@C₂₄ has the highest stabilization energy of -182.87 kcal mol⁻¹ which reflected that designed complexes are thermodynamically stable. The lowest energy gap (G_{H-L}) of 0.83 eV for Mg₄@C₂₄ has reflected its conductive nature. Newly generated HOMO orbitals (due to excess electrons) have dramatically enhanced the NLO response up to 3.62 × 10⁶ au in the case of Mg₄@C₂₄. These results have paved the way to synthesize highly efficient optoelectronic materials (Kosar et al., 2021c).

Transition Metal Doped Nanocages

DFT investigation of second row transition metal atoms (zirconium (Zr), ruthenium (Ru), molybdenum (Mo), and palladium (Pd)) substituted C₂₀ fullerene was carried out. The results manifest that charge distribution of C₂₀ was altered by substitution. The HOMO-LUMO energy gap was lowered in the case of Zr and Mo atoms while it was increased on Ru and Pd substitution. Their nonlinear optical properties including polarizability and hyperpolarizabilities were improved. Their first hyperpolarizabilities were 2795, 2775, 1304, and 66,669 au for Zr, Mo, Ru, and Pd substituted C₂₀ nanocluster (Rad and Ayub, 2017). Scandium (Sc) doped Be₁₂O₁₂, Mg₁₂O₁₂, and Ca₁₂O₁₂ nanocages were explored to study the effect of Sc doping on structure, stability, and optoelectronic properties. Reduction in energy gaps of designed complexes has enhanced conductance of Sc doped complexes. NLO response of all designed complexes was increased and the highest NLO was obtained for Sc-doped Ca₁₂O₁₂. TD-DFT calculations also confirmed that the highest hyperpolarizability was observed

for Sc-doped $\text{Ca}_{12}\text{O}_{12}$ nanoclusters with the smallest transition energy values (ΔE). Sc-doped nanoclusters would be an ideal candidate for optoelectronic devices (Omidi et al., 2017). Exohedral doping of the first row transition metal doping at various sites ($x = b_{64}, b_{66}, r_6,$ and r_4) of $\text{Al}_{12}\text{N}_{12}$ nanocage was carried out. The geometric, electronic, and optoelectronic properties were computed for all $\text{M}@x\text{-Al}_{12}\text{N}_{12}$ complexes and their spin state stability was also computed. Transition metal doping resulted in chemisorption and a remarkable reduction in energy gap up to 40% were observed in this case. Their NLO response was comparable to their alkali metal doped $\text{Al}_{12}\text{N}_{12}$ analogs and the highest NLO response of 1.85×10^4 au was observed for $\text{Cu}@r_6\text{-Al}_{12}\text{N}_{12}$ (Arshad et al., 2018).

Gilani et al. have carried out exohedral and endohedral doping of copper on $\text{Al}_{12}\text{N}_{12}$ nanocages. It was concluded that the $\text{Cu}@r_6\text{-Al}_{12}\text{N}_{12}$ (copper at the center of the six-membered ring of $\text{Al}_{12}\text{N}_{12}$) has the highest reduction in energy gap (E_g) up to 52%. Excess electrons have generated a new HOMO orbital between the original Frontier molecular orbitals as revealed from total and partial densities of states. The highest NLO response of 1.8×10^4 au was observed for $\text{Cu}@r_6\text{-Al}_{12}\text{N}_{12}$ as in the case of previous studies. TD-DFT simulations were performed to obtain crucial excited states. Two level model-based verification of hyperpolarizability was also carried out. These striking results reflect that the designed copper doped complexes would have potential applications in nonlinear optics (Gilani et al., 2018). Ali et al. have explored the exohedral doping of nickel metal (Ni) on inorganic $\text{Mg}_{12}\text{O}_{12}$ nanocluster by using DFT simulations. Different energy changes including zero-point energies (ZPE), thermal enthalpies (ΔH), thermal energies (ΔE), and thermal Gibbs free energies (ΔG) were also computed and compared with interaction energies of $\text{Ni}@r_6\text{-Mg}_{12}\text{O}_{12}$ nanocluster. A remarkably enhanced nonlinear optical response on doping was observed as compared to pristine $\text{Mg}_{12}\text{O}_{12}$ (Rad and Ayub, 2018b). In another work, Rad et al. carried out substitutional doping of transition metal (Cr, Ni, and Ti) at C_{20} fullerene theoretically. Transition metals substitution has altered the charge distribution of C_{20} with the highest charge distribution for TiC_{19} . The nonlinear optical properties were enhanced significantly and the highest hyperpolarizability 2.5×10^3 au observed in the case of TiC_{19} complex (Rad and Ayub, 2018c).

In 2019, the same group also performed the substitutional doping of transition metal (Sc, Fe, Cu, and Zn) at C_{20} fullerene via DFT simulations. Replacement of carbon by a transition metal has enhanced the optoelectronic properties and the highest hyperpolarizability of 2224.5 au was observed for Sc-C_{19} . Furthermore, the results of reactivity descriptors reflected iron-substituted fullerene (Fe-C_{19}) as the softest metal. These results showed that designed transition metal substituted fullerene would have promising applications in optoelectronics (Rad and Ayub, 2019). The optoelectronic effect of the first row transition metal doping $\text{C}_{24}\text{N}_{24}$ cavernous nitride fullerene has been performed via DFT simulation. Transition metal atoms were doped in the N4 cavity of the nanocage. Spin state analysis reflected that spin state stability increases to sextet up to $\text{Mn}@r_4\text{-C}_{24}\text{N}_{24}$ and then gradually decreases to singlet for $\text{Zn}@r_4\text{-C}_{24}\text{N}_{24}$ system. Transition metal atoms have decreased the HOMO-

LUMO energy gap up to 63%. The NLO response was enhanced for all $\text{M}@r_4\text{-C}_{24}\text{N}_{24}$ cavernous nitride complexes and reflected that designed complexes would be better candidates for high performance NLO materials (Shakerzadeh et al., 2020a). The first experimental synthesis of novel all-boron fullerene B_{40} has opened new research avenues for its potential application in various fields (Zhai et al., 2014).

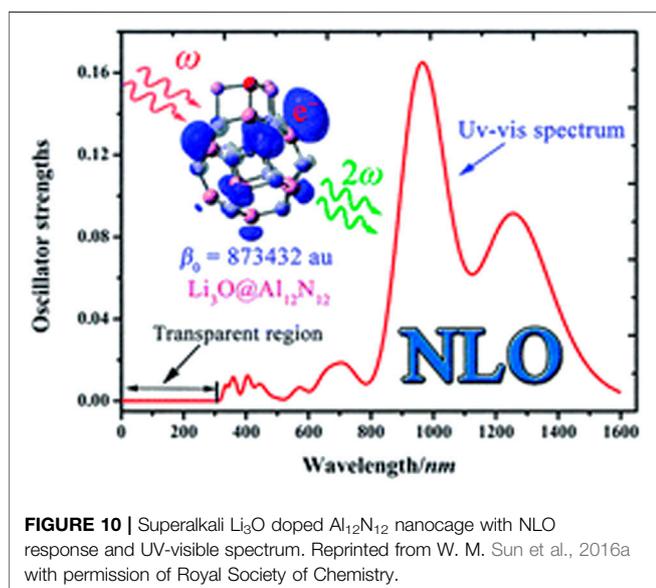
Optoelectronic properties of the first row transition metal decorated at hexagonal and heptagonal rings of B_{40} fullerene have been computed. Obtained complexes were stable with the reduced HOMO-LUMO energy gaps and work functions. The highest hyperpolarizability of 1.35×10^5 au was observed for cobalt (Co) doped B_{40} fullerene (Shakerzadeh et al., 2020b). Ullah et al. investigated the structural and optoelectronic effect of first row transition metals decorated $\text{Al}_{12}\text{P}_{12}$ heterofullerene. Thermally stable $\text{M}@r_4\text{-Al}_{12}\text{P}_{12}$ complexes have reduced energy gaps due to excess electrons of transition metal atoms. Nonlinear optical properties were enhanced and the highest hyperpolarizability up to 5.9×10^6 au was obtained (Ullah et al., 2021). Similarly, optoelectronic properties of transition metal doped $\text{B}_{12}\text{P}_{12}$ nanocage at different doping sites have been explored via DFT simulations. Adsorption of the first row transition metals at $\text{B}_{12}\text{P}_{12}$ have significantly enhanced the thermodynamic stability with the highest interaction energy of $-74.42 \text{ kcal mol}^{-1}$ for $\text{Ni}@r_4\text{-B}_{12}\text{P}_{12}$ nanocluster. Their NLO response has improved remarkably up to 4.4×10^4 au due to excess electron of transition metals. Furthermore, SHG and EOPE values of 1.1×10^5 and 4.4×10^5 au for $\text{Sc}@r_4\text{-B}_{12}\text{P}_{12}$ showed that designed $\text{M}@r_4\text{-B}_{12}\text{P}_{12}$ have a tendency to serve as NLO materials (Irshad et al., 2021). Recently, Khaliq et al. investigated the NLO properties of lanthanum metal doping on $\text{Al}_{12}\text{N}_{12}$ and $\text{Al}_{12}\text{P}_{12}$ nanoclusters. Interaction energy analysis indicated that designed complexes were stable and exohedral doping was more favorable than endohedral doping. Lanthanum doping has uplifted the NLO responses of complexes up to 4.43×10^4 au and will serve as a high-tech NLO material in optoelectronics (Khaliq et al., 2021a). The highest nonlinear optical response of some alkali metal doped nanocages is listed in Table 4.

Superalkali Doped Nanocages

Superalkalis have low ionization potential than alkali metals and have a better tendency to donate excess electrons toward the system (Gutsev and Boldyrev, 1982). This enables them to form a wide range of unique molecules with intriguing features while the structural integrity of superalkalis remains intact on interaction with other atoms. In this regard, superalkalis (Li_2F , Li_3O , and Li_4N) (Rehm et al., 1992), hyperlithiated superalkali clusters Li_nF ($n = 2-5$) (Srivastava and Misra, 2015c), and hypervalent superalkalis M_2X ($\text{M} = \text{Li}, \text{Na}; \text{X} = \text{F}, \text{Cl}$) (Srivastava and Misra, 2016c) served as potential superalkali subunits. These superalkali clusters on interaction with metal atoms resulted in the formation of hyperalkalized superalkali-metal (SA-M) species (Srivastava and Misra, 2016b). These species possess remarkable NLO response and the highest NLO up to 3.6×10^4 au is observed for $\text{NLi}_4\text{-Na}$. The gas phase basicities of superalkali hydroxides FLi_nOH ($n = 2-5$) have been computed theoretically and are

TABLE 4 | Transition metal doped nanocages with enhanced nonlinear optical responses.

Complex	Hyperpolarizability (au)	Software	Level of theory	References
Pd-C ₁₉	6.6×10^4	Gaussian	ω B97XD/ 6-311G (d,p) for C and LANL2DZ for Pd	Rad and Ayub. (2017)
Sc-Ca ₁₁ O ₁₂	2.9×10^5	Gaussian	CAM-B3LYP/ 6-31+G(d)	Omid et al. (2017)
Cu@r ₆ -Al ₁₂ N ₁₂	1.8×10^4	Gaussian	CAM-B3LYP/ 6-311+G(d)	Gilani et al. (2018)
M@Mg ₁₂ O ₁₂	1.2×10^3	Gaussian	ω B97XD/6-311G+(d,p)	Rad and Ayub, (2018b)
Ti-C ₁₉	2.5×10^3	Gaussian	LC- ω B97XD/6-311 + G(d)	Rad and Ayub, (2018c)
Co@B ₄₀	1.3×10^5	Gaussian	CAM-B3LYP/ 6-31+G(d)	Shakerzadeh et al. (2020b)
Co@b ₆₄ -Al ₁₂ P ₁₂	5.9×10^6	Gaussian	CAM-B3LYP/ 6-311+G(d)	Ullah et al. (2021)
Sc@r ₄ -B ₁₂ P ₁₂	4.4×10^4	Gaussian	CAM-B3LYP/ 6-311+G(d)	Irshad et al. (2021)



comparable to those of strong alkali hydroxides such as LiOH and some of them may act as superbases (Srivastava and Misra, 2015a). These superalkali hydroxides have several unusual and intriguing features, one of which is their enhanced NLO responses. The hydrogenated superalkalis (SAHs = FLi₂H, OLi₃H, and NLi₄H) with enhanced NLO response have also been investigated theoretically (Srivastava and Misra, 2016a).

These superalkali clusters donate their excess electrons on interaction with nanocages to form high performance NLO materials. In 2016, Sun et al. carried out theoretical investigation of superalkali M₃O (M = Li, Na, K) doping on Al₁₂N₁₂ nanocage for the first time (W. M. Sun et al., 2016a). Diffuse excess electrons of superalkalis have enhanced the hyperpolarizability of complexes up to 1.86×10^7 au. Moreover, NLO response of Li₃O superalkali on other nanocages has been investigated systematically. These electrides have high deep ultraviolet transparency and larger NLO response. These superalkali doped nanocages would be

potential precursors for high-performance NLO materials as shown in **Figure 10**.

The optoelectronic properties of superalkali M_nO (M = Li, Na, K; n = 2, 3, 4) doped Mg₁₂O₁₂ nanocages have been investigated theoretically. Superalkali excess electrons have reduced the energy gap and remarkable increment in the NLO response was observed for M₃O superalkali doped nanocluster series. These complexes were potential candidates in the field of nonlinear optics with the highest hyperpolarizability of $\beta \approx 600,000$ au for K₃O@Mg₁₂O₁₂ complex (Hesari et al., 2016). In another work, Li₃O, Na₃O, and K₃O doped Si₁₂C₁₂ nanocages have been explored via DFT simulations. It was observed that energy gap (HOMO-LUMO) was reduced monotonically with the size of superalkali subunits. Doping of superalkalis Li₃O@Si₁₂C₁₂ (3.750 eV), Na₃O@Si₁₂C₁₂ (2.984 eV), and K₃O@Si₁₂C₁₂ (2.634 eV) has transformed the pristine Si₁₂C₁₂ nanocage (5.452 eV) to n-type semiconductors. A reduction in HOMO-LUMO gap has strikingly enhanced the NLO response with the highest hyperpolarizability of 21,695 au for K₃O@Si₁₂C₁₂. These superalkali doped Si₁₂C₁₂ nanocages would have a major role in optoelectronic devices due to their semiconducting nature (Lin et al., 2017). Nonlinear optical properties of superalkali doped C₂₀ fullerene like nanocluster have been investigated theoretically. A decrement in energy gap was observed and indicated that superalkalis have enhanced the optoelectronic properties of C₂₀ fullerene. A large NLO response was observed with the highest hyperpolarizability for Na₃O@C₂₀ nanocluster (Noormohammadbeigi and Shamlouei, 2018). Inorganic boron-based nanosystem of all-boron fullerene B₄₀ has also been doped with superalkali subunits (M₃O)_n (M = Li and K, n = 1 and 2) to investigate the geometrical, stability, and optoelectronic properties. Excess electrons of superalkalis have significantly enhanced the NLO response and narrowed the HOMO-LUMO energy gap (0.61–1.11 eV) as compared to pristine B₄₀ (2.86 eV). The increment in the first hyperpolarizability and second hyperpolarizability was up to 2.46×10^5 and 4.85×10^8 au, respectively. These complexes were structurally stable due to formation of B-O bond and have binding energies in the range of 57.0–99.8 kcal/mol. Their fascinating results reflect that superalkali doped B₄₀

nanocage would be beneficial for modern electronic nanodevices (Noormohammadbeigi and Shamlouei, 2018).

In 2019, Ullah et al. carried out three superalkalis doping on Li_2F , Li_3O , and Li_4N on fullerene like $\text{B}_{12}\text{P}_{12}$ inorganic nanocage to investigate the NLO response of designed complexes. Doping at various sites resulted in different isomers with excess electrons and were thermodynamically stable. Nonlinear optical response of complexes has been enhanced with the highest hyperpolarizability of 3.48×10^5 au. These superalkali doped $\text{B}_{12}\text{P}_{12}$ nanoclusters have deep ultraviolet transparency and would have potential applications in high-performance NLO devices (Ullah et al., 2019a). In the same year, theoretical investigation of Li_2F , Li_3O , and Li_4N doping on $\text{B}_{12}\text{P}_{12}$ nanocage have been carried out to observe their geometric, electronic, and NLO properties. All the designed complexes were electride in nature due to diffuse excess electrons of superalkali subunits. These complexes were highly stable as indicated by their interaction energies ($-105.13 \text{ kcal mol}^{-1}$). These stable inorganic electrides have narrowed HOMO-LUMO energy gap with an increment in NLO response up to 6.25×10^4 au for $\text{Li}_4\text{N}@Al_{12}P_{12}$ (Ullah et al., 2019b). Ullah et al. also explored the superalkali (Li_2F , Li_3O , and Li_4N) doping on $\text{Si}_{12}\text{C}_{12}$ nanocage at various positions via DFT calculations. Superalkali doping has altered the electronic properties of $\text{Si}_{12}\text{C}_{12}$ from insulator to n-type semiconductor. These complexes have static first hyperpolarizability up to 19,864 au. Furthermore, frequency dependent hyperpolarizability calculations were also performed in the region 400–1600 nm to check their practical applicability. The designed complexes were transparent in deep UV regions and would be applicable in the deep UV transparent NLO materials (Ullah et al., 2020d). In a recent work, Li_3O , Na_3O , and K_3O superalkalis doping at various doping sites of $\text{Zn}_{12}\text{O}_{12}$ nanocage have been carried out theoretically. Excess electrons of superalkalis have enhanced the NLO response of $\text{Zn}_{12}\text{O}_{12}$ nanocluster and were UV transparent under workable laser conditions. The NLO increased monotonically and the highest NLO response of 394,217 au was observed for $\text{K}_3\text{O}@Zn_{12}O_{12}$. These n-type semiconductor complexes have reduced the energy gap up to 70% as compared to pristine $\text{Zn}_{12}\text{O}_{12}$. These designed complexes will be applicable in the high performance NLO materials (Kosar et al., 2020b).

A theoretical investigation of superalkali doping on structural and optoelectronic properties of C_{24} fullerene has been carried out via DFT simulations. The density of states analysis was carried out to confirm the alteration in HOMO-LUMO energy gap on superalkalis doping. The excess electrons of superalkalis have remarkably enhanced the NLO response especially polarizability and hyperpolarizability of C_{24} fullerene-based nanostructures (Omidi et al., 2020). Li_3O super alkali doping at various positions of $\text{B}_{12}\text{N}_{12}$ reflected that designed complexes were thermodynamically stable and chemisorbed. A remarkable reduction in HOMO-LUMO energy gap (0.42–3.94 eV) has transferred the designed complexes to n-type semiconductor as compared to pristine insulator nanocage (6.84 eV). Nonlinear optical response of superalkali doped $\text{B}_{12}\text{N}_{12}$ nanocluster was increased from 1045 au to 126,261 au. These

complexes were transparent in the UV region as reflected by TD-DFT investigations and would have practical applications as optoelectronic materials (Raza Ayub et al., 2020). In a recent work, Li_4N and Li_4O doped $\text{Al}_{12}\text{N}_{12}$ nanoclusters have been explored for their NLO properties (Khaliq et al., 2021b). These Li_4N and Li_4O based $\text{Al}_{12}\text{N}_{12}$ nanoclusters were thermodynamically stable and have deep UV transparency. Smaller excitation energies of 1.27–2.73 eV have a major role in tuning up the NLO response of designed complexes. A remarkable enhancement in NLO response with the highest hyperpolarizability of 5.7×10^4 au was achieved for $\text{Li}_4\text{N}@Al_{12}N_{12}$ isomer (Figure 11). These Li_4N and Li_4O based $\text{Al}_{12}\text{N}_{12}$ nanoclusters would be potential precursors in designing high-performance NLO materials.

Excess Electron Based Organic Complexes

Besides inorganic nanoclusters, superalkali doping on many other organic clusters has been carried out for their potential applications in nonlinear optics (X. Li and Li, 2019) (P. Khan et al., 2021a). Organic NLO materials have extended π conjugation, high laser damage thresholds, and smaller dielectric constants (Kang et al., 2019). Most of these organic NLO materials are electrides, alkalides, alkaline earthides, coinage metalides, and superalkalides and have been described in the above sections. However, some other superalkali doped organic NLO materials have attracted much attention in recent years. In this regard, the NLO response of M_3O and M_3S ($\text{M} = \text{Li}, \text{Na}, \text{and K}$), single and double superalkali M_3O doped graphdiyne nanoclusters have been explored (N. Hou et al., 2021; Kosar et al., 2020b; X. Li et al., 2020b). Similarly, Shehzadi et al. observed a remarkable increase in the NLO response of superalkali doped graphdiyne nanoclusters ($\text{M}_2\text{X}@GDY$ $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and $\text{M} = \text{Li}, \text{Na}, \text{K}$) with the highest response (7.7×10^4 au) for $\text{Na}_2\text{F}@GDY$ (Shehzadi et al., 2019). Such novel carbon material graphynes (GYs) on combination with superalkalis results in the formation of stable complexes. These GY superalkali complexes $\text{OM}_3^+@(\text{GY}/\text{GDY}/\text{GTY})^-$ possess exceptionally large NLO response of 6.5×10^5 au for $\text{Li}_3\text{O}@GTY$ (GTY = graphtrigne). The NLO properties of doping of alkali metal atoms and superalkali at pyridinic vacancy graphene (3NG) have been studied theoretically. The highest NLO response of 1.6×10^4 was observed for $\text{K}_3\text{O}@3\text{NG}$ (Song et al., 2018b). A theoretical exploration of superalkali doped boron substituted biphenalenyl diradical dimer ($\text{BC}_{25}\text{H}_{18}$) was carried out by Song et al. and the highest NLO response was for $\text{K}_3\text{O}@BC_{25}H_{18}$ (Song et al., 2018a). Superalkali doping on cyclic conjugated ring systems especially cyclic oligofuran (CF) and hexathiophene ring (6CT) has been carried out theoretically to evaluate their NLO response (Sajid et al., 2020; Sajid et al., 2021). The highest NLO response of some organic complexes is listed in Table 5.

NONLINEAR OPTICAL RESPONSE: EXPERIMENTAL VS. THEORETICAL

The corroboration between theoretical and experimental data is useful for designing and synthesis of novel NLO materials. In this regard, various NLO systems have been synthesized and their

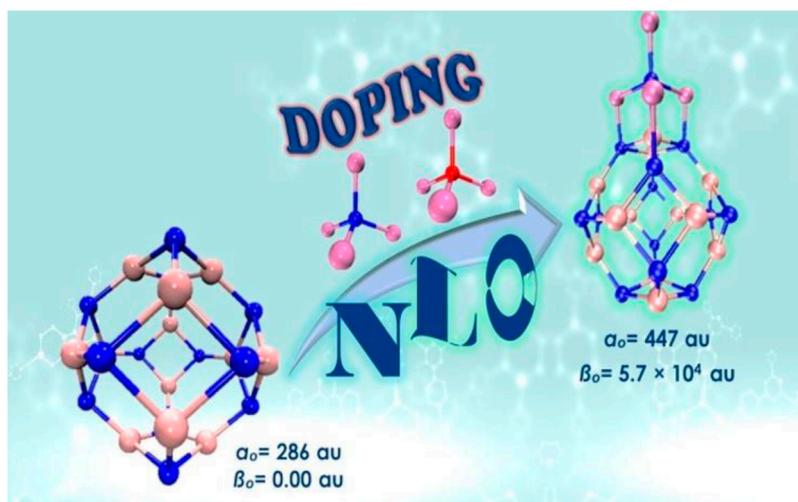


FIGURE 11 | $\text{Li}_4\text{N@Al}_2\text{N}_{12}$ complex with the highest hyperpolarizability of 5.7×10^4 au. Reprinted from Khaliq et al., 2021b with permission from Elsevier.

TABLE 5 | Some superalkali doped organic complexes with enhanced nonlinear optical response.

Complex	Hyperpolarizability (au)	Software	Level of theory	References
$\text{Na}_3\text{S@GDY}$	1.36×10^5	Gaussian	LC-BLYP/ 6-311G (d,p)	Kosar et al. (2020b)
$\text{Na}_2\text{F@GDY}$	7.7×10^4	Gaussian	LC-BLYP/ 6-31G+(d,p)	Shehzadi et al. (2019)
$\text{K}_3\text{O@3NG}$	1.6×10^4	Gaussian	CAM- BhandHLYP/6-31+G (d)	Song et al. (2018b)
$\text{K}_3\text{O@GDY}$	3.06×10^5	Gaussian	CAM-B3LYP/ 6-311++G (2days, 2p)	X. Li et al. (2020b)
$\text{K}_3\text{O@GDY}$	2.7×10^5	Gaussian	CAM-B3LYP/ 6-31+G(d)	N. Hou et al. (2021)
$\text{Li}_3\text{O@GTY}$	6.5×10^5	Gaussian	CAM-B3LYP/ 6-31+G(d)	N. Hou et al. (2021)
$\text{K}_3\text{O@C}_{104}\text{H}_{52}$	1.7×10^5	Gaussian	CAM-B3LYP/ 6-31+G(d)	Kosar et al. (2021a)
$\text{K}_3\text{O@nCF}$	5.1×10^7	Gaussian	LC-BLYP/ 6-31+G (d,p)	Sajid et al. (2020)
$\text{K}_3\text{O@BC}_{25}\text{H}_{18}$	1.1×10^4	Gaussian	BhandHLYP/ 6-31+G (d)	Song et al. (2018a)
$\text{Na}_3\text{O@6CT}$	5.0×10^4	Gaussian	LC-BLYP/ 6-31+G (d,p)	Sajid et al. (2021)

NLO responses have been investigated theoretically and experimentally. The linear and NLO susceptibilities of single crystals of potassium titanyl phosphate KTiOPO_4 have been studied experimentally and theoretically (Reshak et al., 2010). Using DFT calculations, the theoretically predicted band gap (3.1 eV) of KTiOPO_4 shows excellent agreement with the experimental data (3.2 eV) at WIEN2K code. Furthermore, the computed second harmonic generation (SHG) susceptibility coefficients are matched with single crystal SHG response. The experimental and theoretical NLO studies of synthesized $\text{LiBaB}_9\text{O}_{15}$ crystals have been carried out (Reshak et al., 2013). The electronic properties especially band gap energies (5.11 eV) by using DFT simulations match well with the experimental values (5.17 eV). The calculated second order NLO susceptibility

especially second harmonic generation (SHG) was $\beta_{333} = 0.291 \times 10^{-30}$ esu at 1064 nm. This computed value correlated with the experimental one (0.467×10^{-30} esu) at 1064 nm by using Nd:YAG laser. Single crystals of LiNaB_4O_7 have been synthesized and confirmed by X-ray crystallography. The results of DFT calculations for electronic properties by using LDA, GGA, EVGGA, and mBJ methods demonstrate that these crystals have a substantial band gap of about 2.80, 2.91, 3.21, and 3.81 eV, respectively. These results match well with the experimental band gap of 3.88 eV. The calculated absorption spectrum of LiNaB_4O_7 crystals also matched well with the experimental one. The second order hyperpolarizabilities of these crystals were 0.306×10^{-30} esu (static) and 0.332×10^{-30} esu at 1064 nm (Reshak et al., 2012). The first and

second hyperpolarizabilities of substituted dimesityl boranes have been explored both theoretically (AM1 semi-empirical level, MOPAC program) and experimentally (at 1907 nm under Nd-YAG laser). The theoretical results were in concurrence with the experimentally measured data for these complexes (Yuan et al., 2006). The nonlinear optical crystals of strontium borate $\text{Sr}_2\text{B}_5\text{O}_9(\text{OH})\text{H}_2\text{O}$ have been synthesized. The DFT calculations of SHG response, nonlinear refractive index, and birefringence computed by using CASTEP package were consistent with experimentally measured values (Zhang et al., 2015). These studies show that theoretical strategies for calculating NLO response show a good agreement with the available experimental data. Therefore, theoretically predicted high performance NLO materials could be a good starting point for the experimentalists.

CONCLUSION AND OUTLOOK

The current review establishes a systematic array of different studies for the theoretical designing of NLO materials. NLO materials have covered a large area of science and technology owing to their potential applications in optoelectronics. In material research, computational design and experimental synthesis of NLO materials with higher order nonlinearities come into vogue. Several strategies including metal ligand framework, push pull mechanism, diradical character, and so on have been elaborated for the enhancement of NLO response of materials. Role of diffuse excess electron in developing noncentrosymmetric materials for nonlinear optics have been discussed. A theoretical design from the simplest NLO material to

the complex alkali, alkaline earth, transition, and superalkali doped nanoclusters is summarized in the present review. Excess electrons of the nanoclusters have played a pivotal role in enhancing the NLO properties of various systems especially hyperpolarizabilities. These excess electron-based systems may help to increase the second harmonic generation (SHG) efficiency and electro-optical Pockels effect (EOPE). These insights are essential for the development of new NLO materials. These findings also provide an intriguing area for future research into potential building blocks and structure-directing constituents that may help to promote the synthesis of these theoretically designed NLO materials. It is expected that the present review will provide a better understanding of the NLO responses of nanoclusters, paving the way for the development of high-tech NLO materials.

AUTHOR CONTRIBUTIONS

K.A., M.G., and T.M. contributed to the design and outlines of the review. R.B. and M.A. collected the literature and wrote the first draft. R.Z. revised the first draft and corrected its language. J.I. and S.T. wrote some sections of the review. All authors contributed to manuscript revision, read, and approved the submitted version.

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